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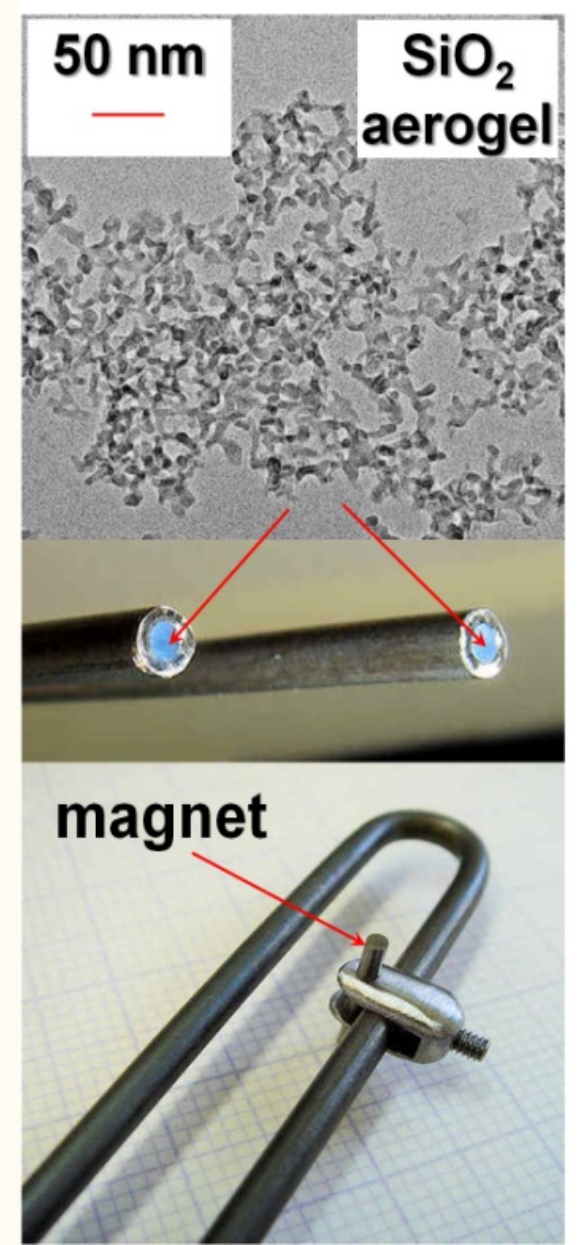
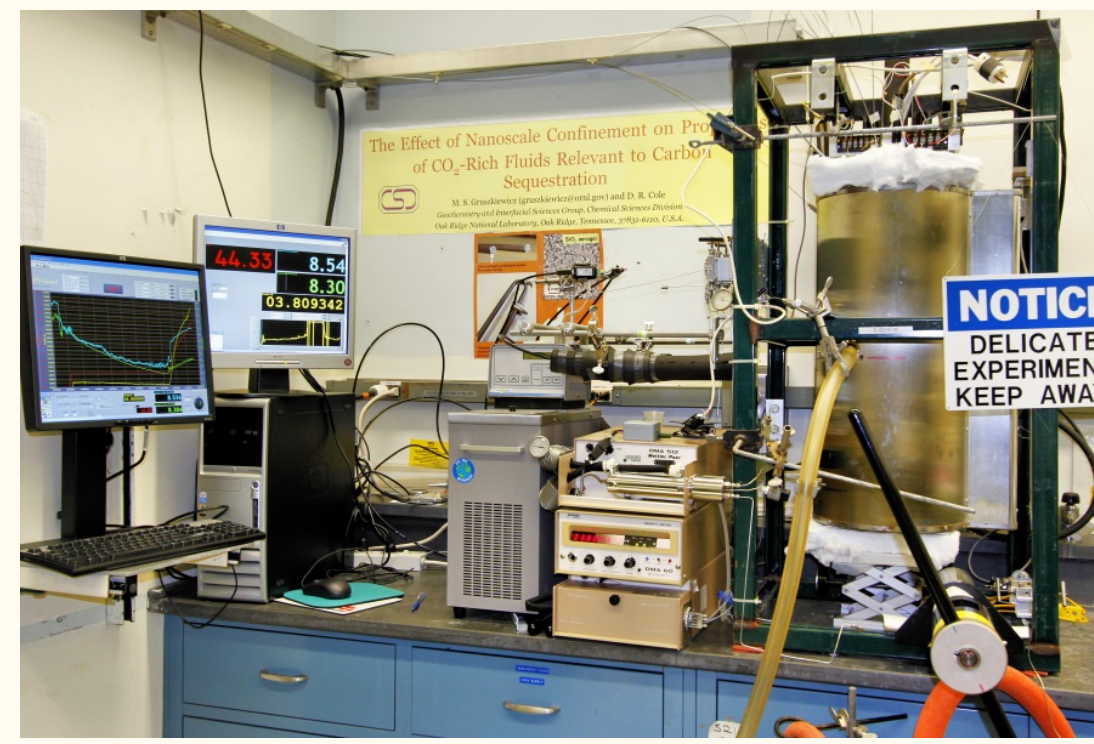
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DENSITIES AND VAPOR-LIQUID EQUILIBRIA BY VIBRATING TUBE DENSIMETRY

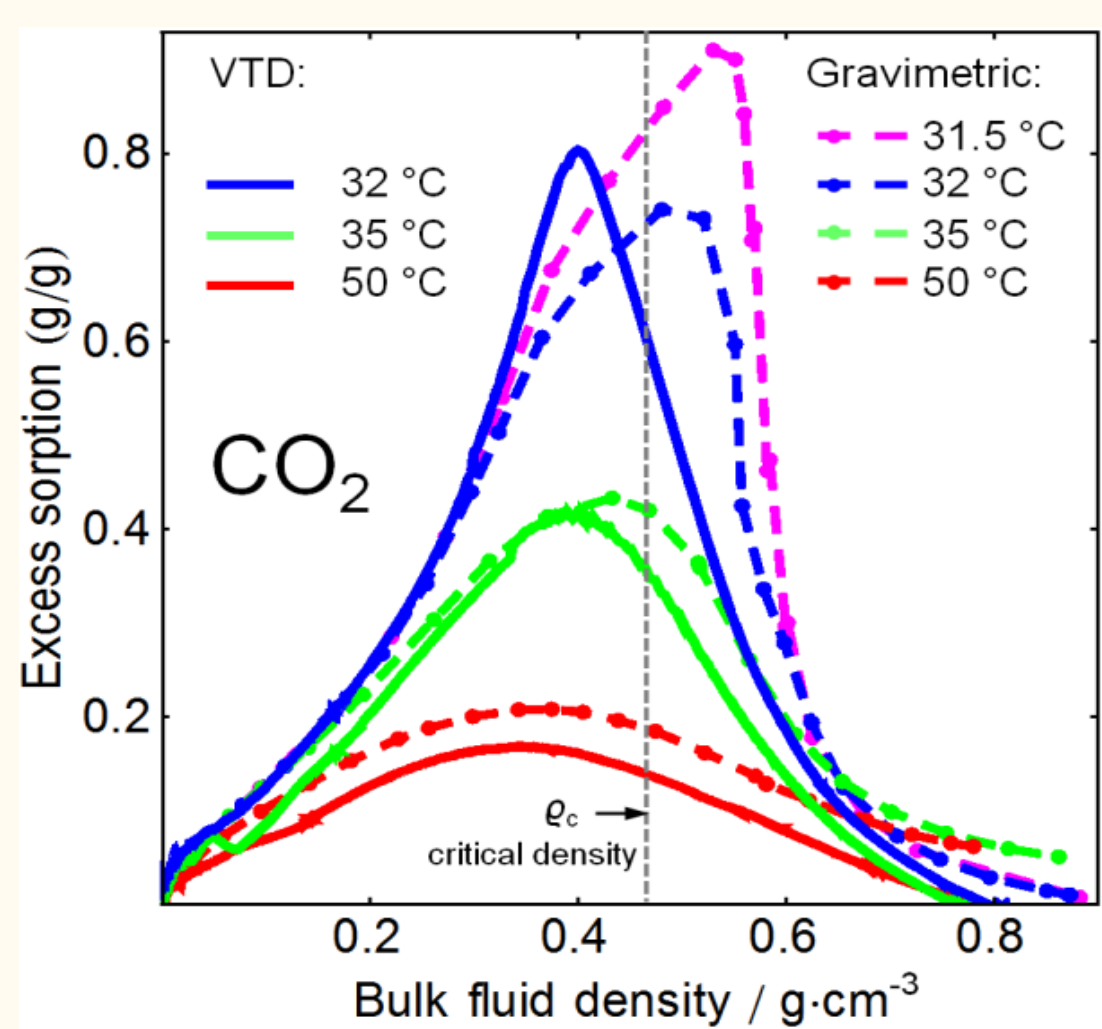
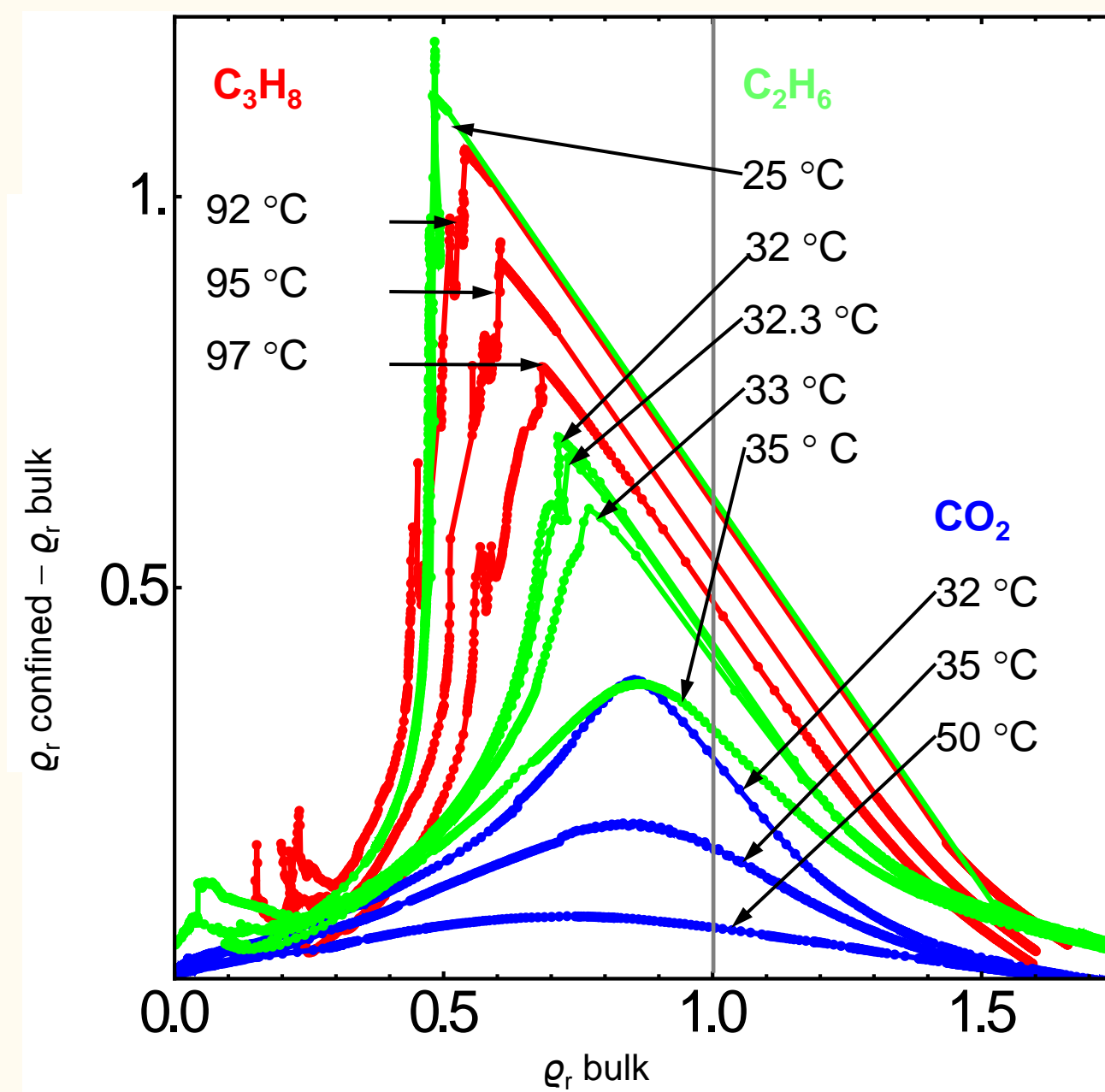
**Objective:** Develop a new VTD approach suitable for investigation of dense pore fluids and mixtures

- Densities of pore-confined fluids at near-critical and supercritical conditions were measured for the first time using VTD.<sup>1</sup>
- Measurements yield total adsorption capacity via a novel approach, complementary to traditional gravimetric/volumetric adsorption methods.

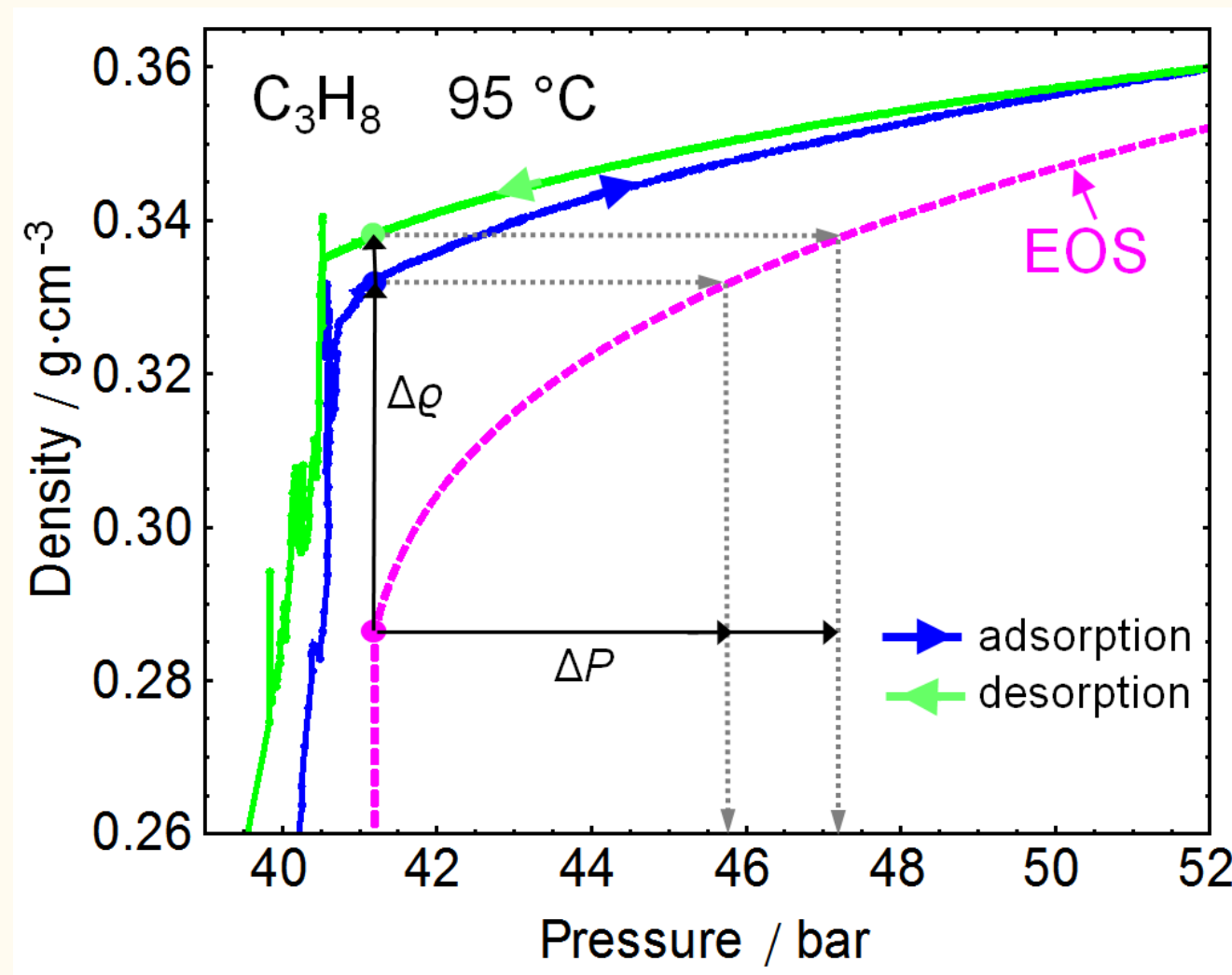


Monolithic hydrophobic SiO<sub>2</sub> aerogel ( $\rho = 0.2$  g/cm<sup>3</sup>; 90% porosity; 7 to 9 nm mesh strands) was synthesized inside 1/8" Hastelloy U-tubes.

Reduced excess density of ethane, propane, and CO<sub>2</sub> at subcritical and supercritical conditions as a function of the reduced density of the bulk fluid. Excess density peaks below the critical density and persists far above the critical temperature.



The excess sorption VTD results for pure CO<sub>2</sub> in SiO<sub>2</sub> aerogel show large excess sorption peaks which are similar, but not identical with gravimetric results around the critical density and at high pressure.



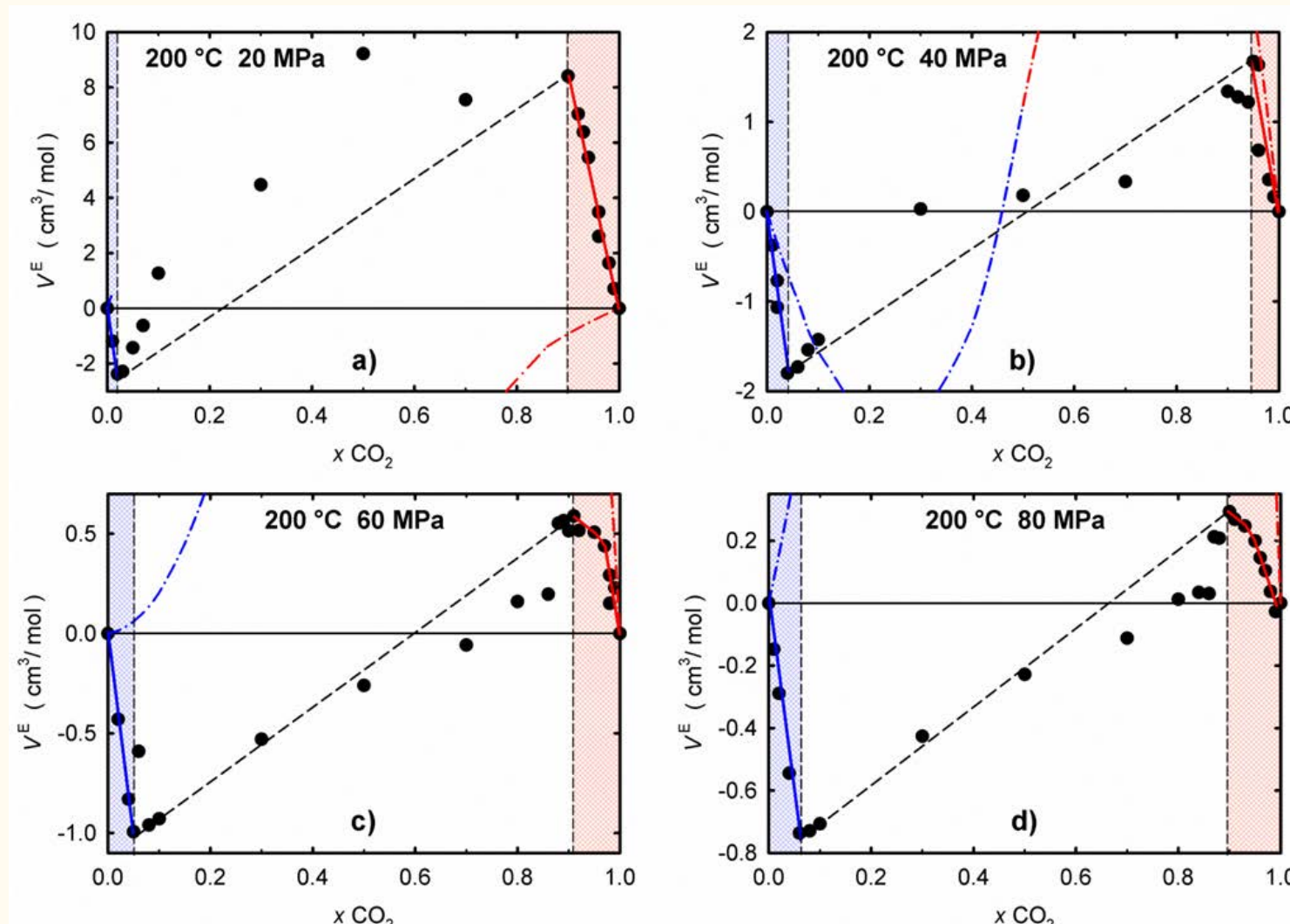
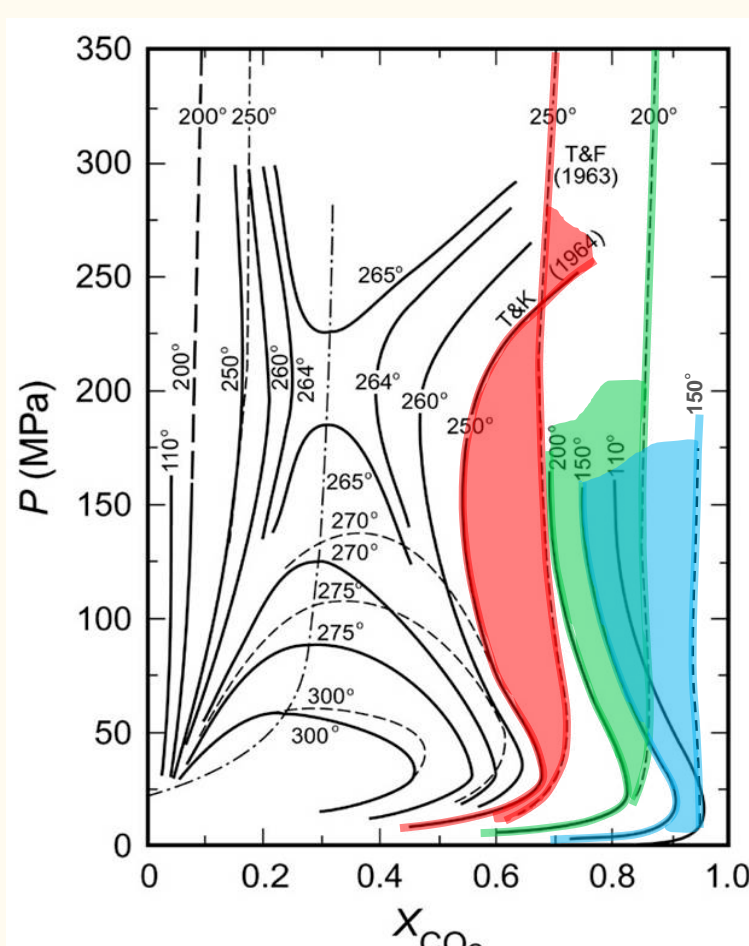
VTD isotherms of adsorption clearly demonstrate the densification of the pore fluid (propane) in comparison with the bulk fluid at the same pressure.

Densities and vapor-liquid equilibria of CO<sub>2</sub> + H<sub>2</sub>O in the CO<sub>2</sub>-rich region:

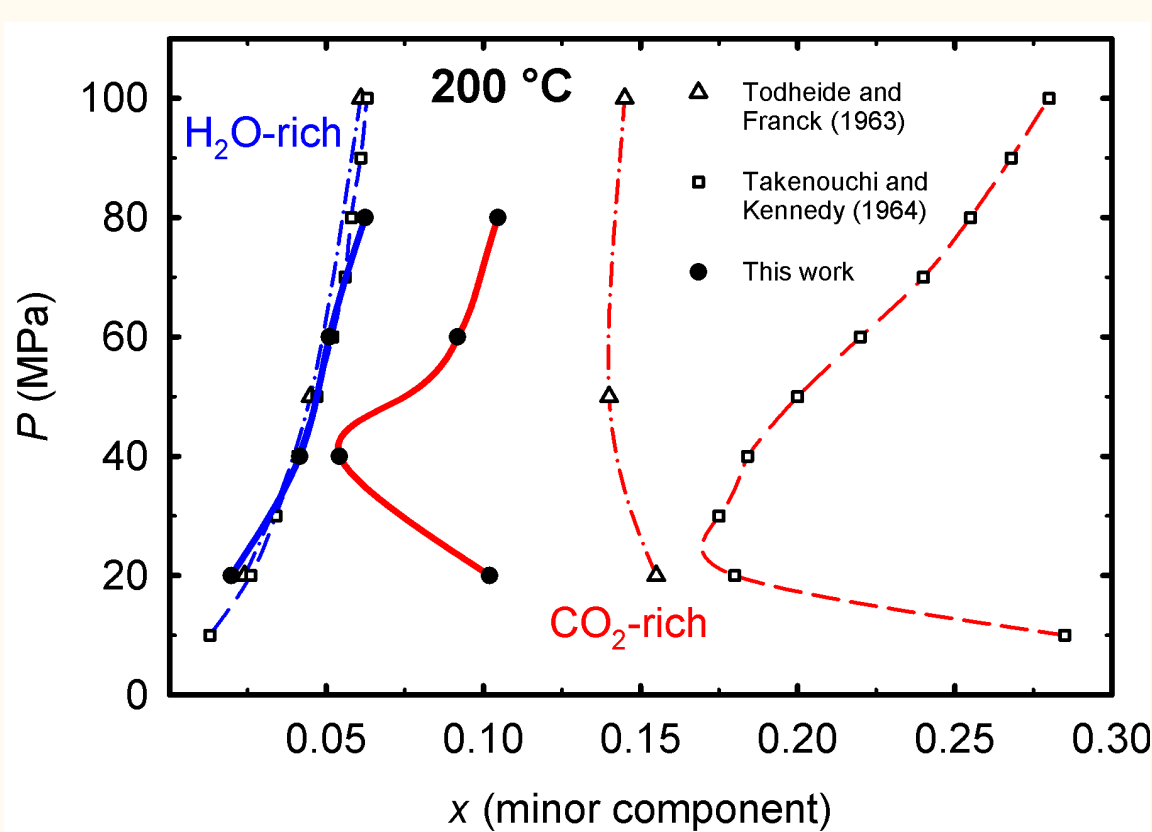
**Objective:** Advance the development of an accurate equation of state for CO<sub>2</sub> + H<sub>2</sub>O needed for energy applications by reducing large discrepancies in experimental data for this important mixture (e.g. solubility of water in CO<sub>2</sub>).



- New measurements were made by VTD to 250 °C and 100 MPa.
- Fluid phase boundaries, essential for development of equations of state, can be detected from the changes of excess volume as a function of composition or from oscillation frequency patterns.



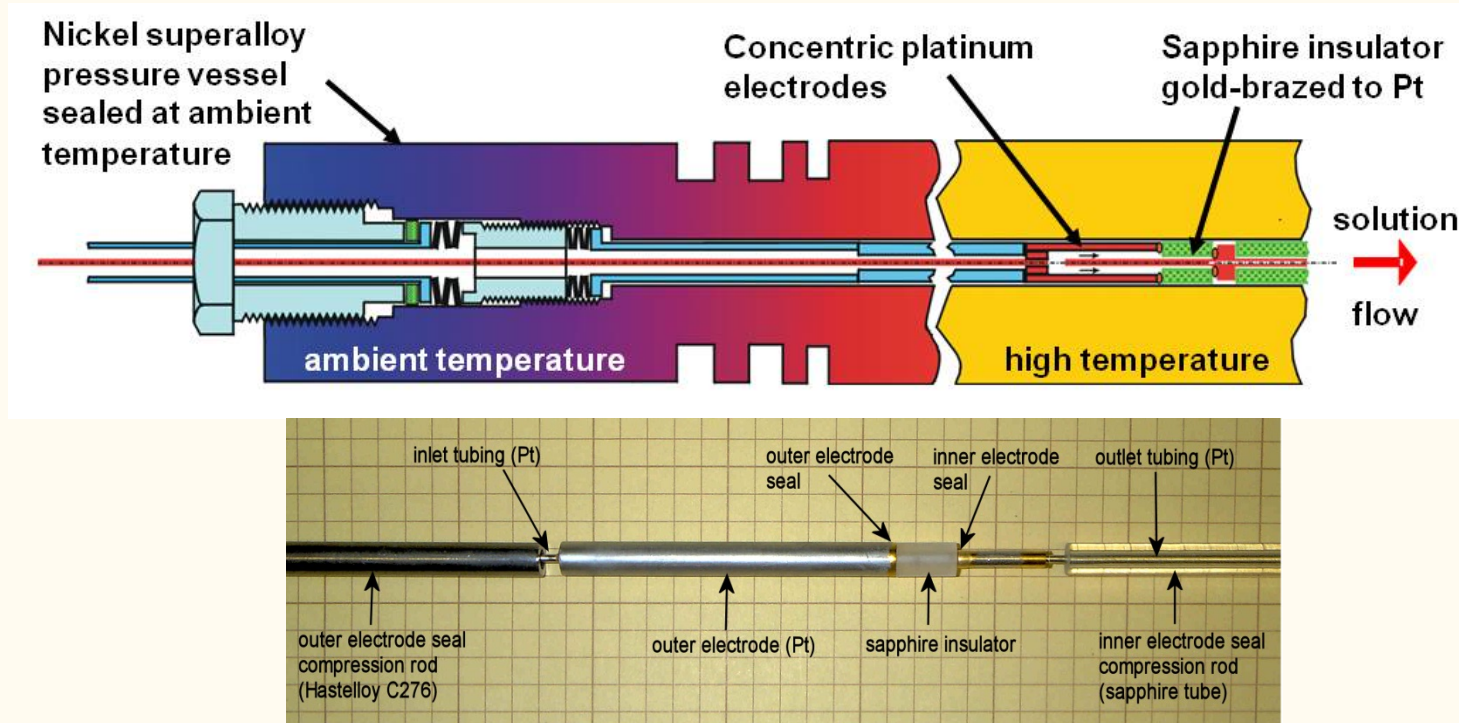
Excess molar volumes of CO<sub>2</sub> + H<sub>2</sub>O at 200 °C compared with predictions using existing universal equation of state (REFPROP)



The new phase boundaries agree very well with literature data in the water-rich region, but for the CO<sub>2</sub>-rich phase are significantly different from the two well-known earlier comprehensive studies. Accurate experimental data will improve both empirical and molecular-level modeling of CO<sub>2</sub>-rich fluids.

ELECTROLYTIC CONDUCTIVITY TO 700 °C, 100 MPa

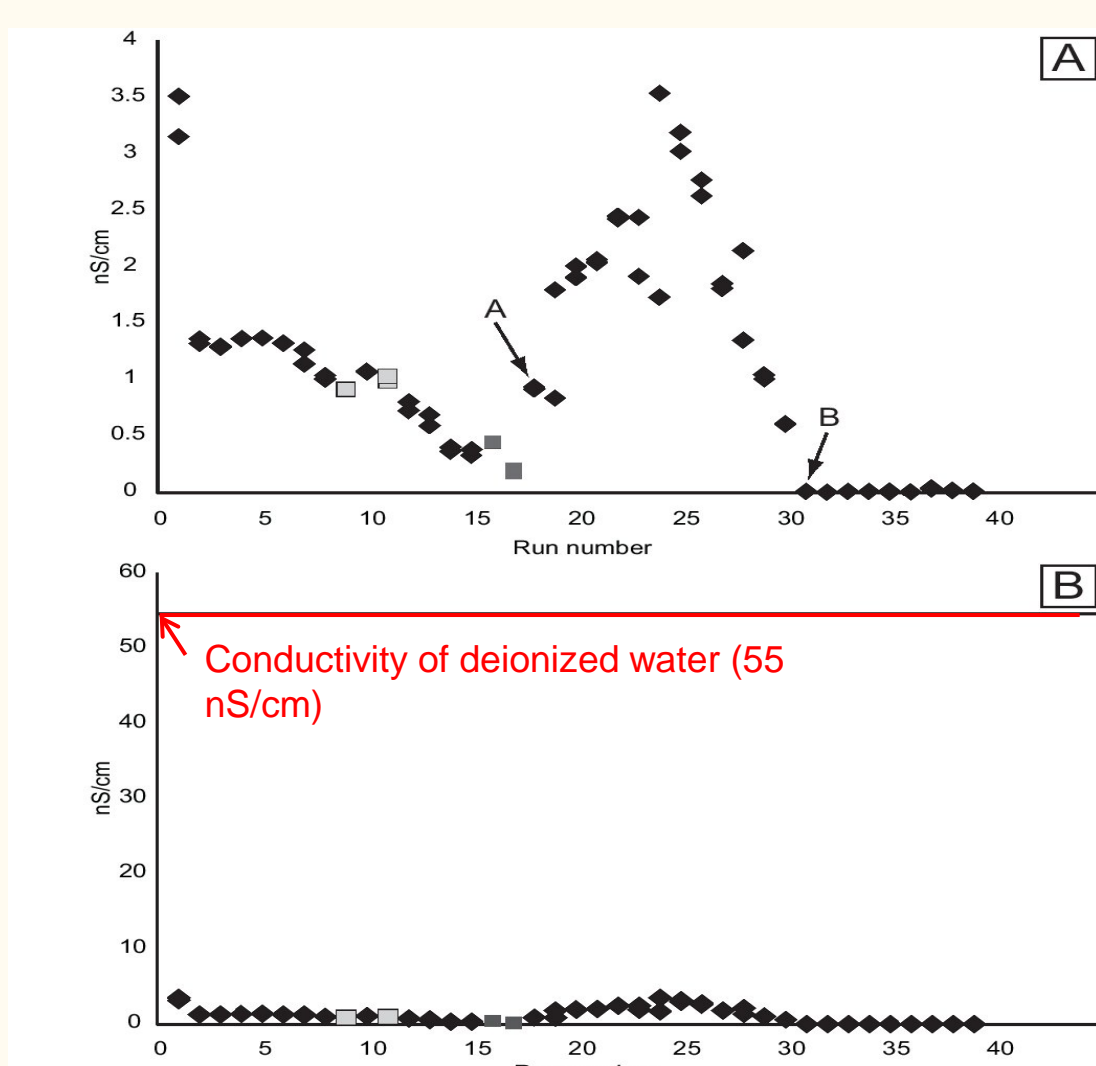
Ionic conductance is an excellent probe of ion-solvent interactions. Measurements in extremely dilute solutions (in the limiting law region) yield ion mobilities and association constants independent of additional assumptions. The required high sensitivity is possible only with flow cells built of non-corrosive materials to maintain high purity.



The new ORNL fluid-flow conductivity cell enclosed in a nickel alloy pressure vessel with concentric Pt electrodes, and zero-pressure Pt-gold-sapphire seals at high temperature. The fluid-flow design and the material selection enable measurements on very dilute solutions (<10<sup>-6</sup> mol/kg) with high sensitivity, even at very high temperature (to 700 °C, 100 MPa).

Recent conductivity results:<sup>2</sup> no ionization in "wet CO<sub>2</sub>":

**Objective:** Investigate the mechanism of the observed high reactivity of CO<sub>2</sub>-rich fluid towards minerals and metals.

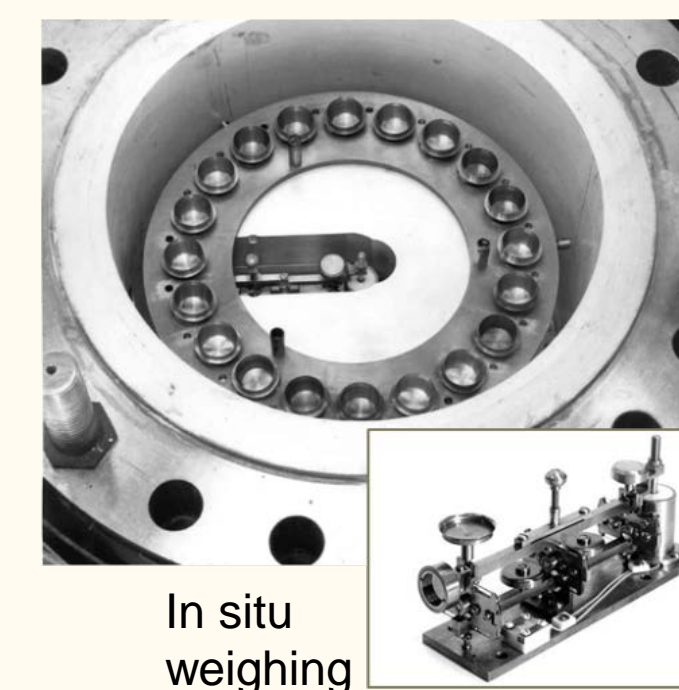


Recent experimental work suggests that CO<sub>2</sub> containing small amounts of dissolved water, corresponding to its solubility at ambient temperature, shows unusually high reactivity towards metals and minerals.

We undertook measurements<sup>2</sup> of the conductivity of such solutions to 200 °C and 20 MPa to detect the presence of ions in "wet CO<sub>2</sub>". The results were negative – the conductivity of CO<sub>2</sub> remained significantly below that of pure deionized water and even below the sensitivity of the method.

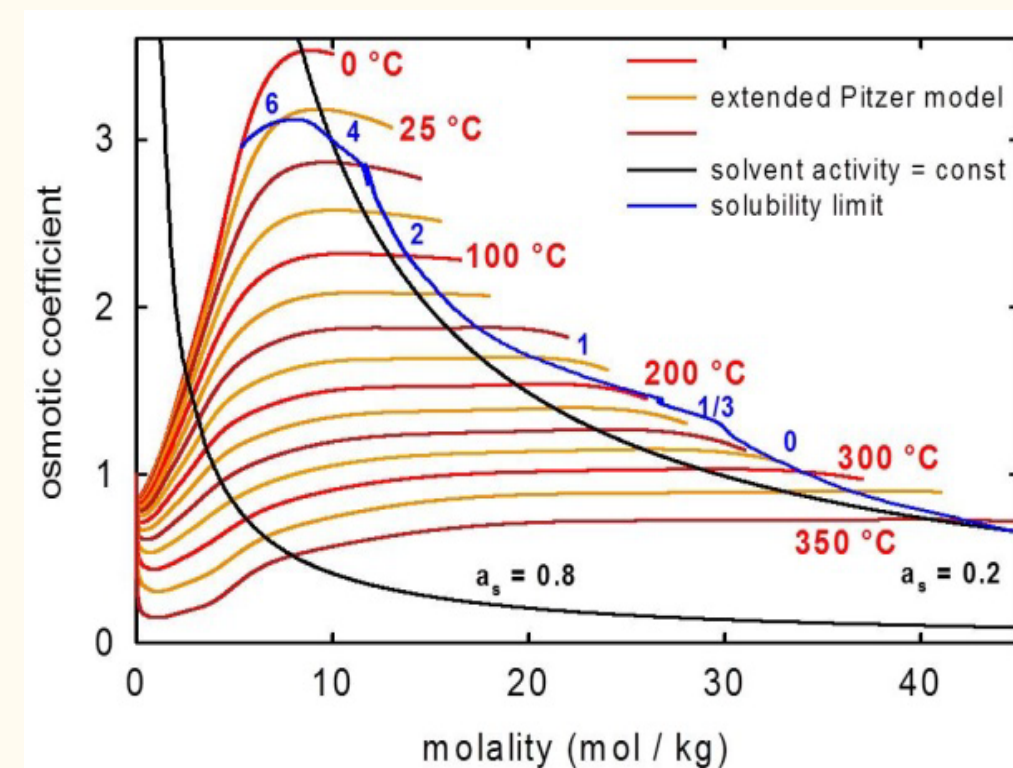
**Conclusion:** There is practically no ionization in the CO<sub>2</sub>-rich phase. The mechanism of the observed reactivity must be different from that seen in the water-rich phase. It is possible that water concentrates preferentially in CO<sub>2</sub>-saturated thin layers at the solid-fluid interface.

SOLUTE ACTIVITIES AND WATER SORPTION IN POROUS SOLIDS TO 250 °C



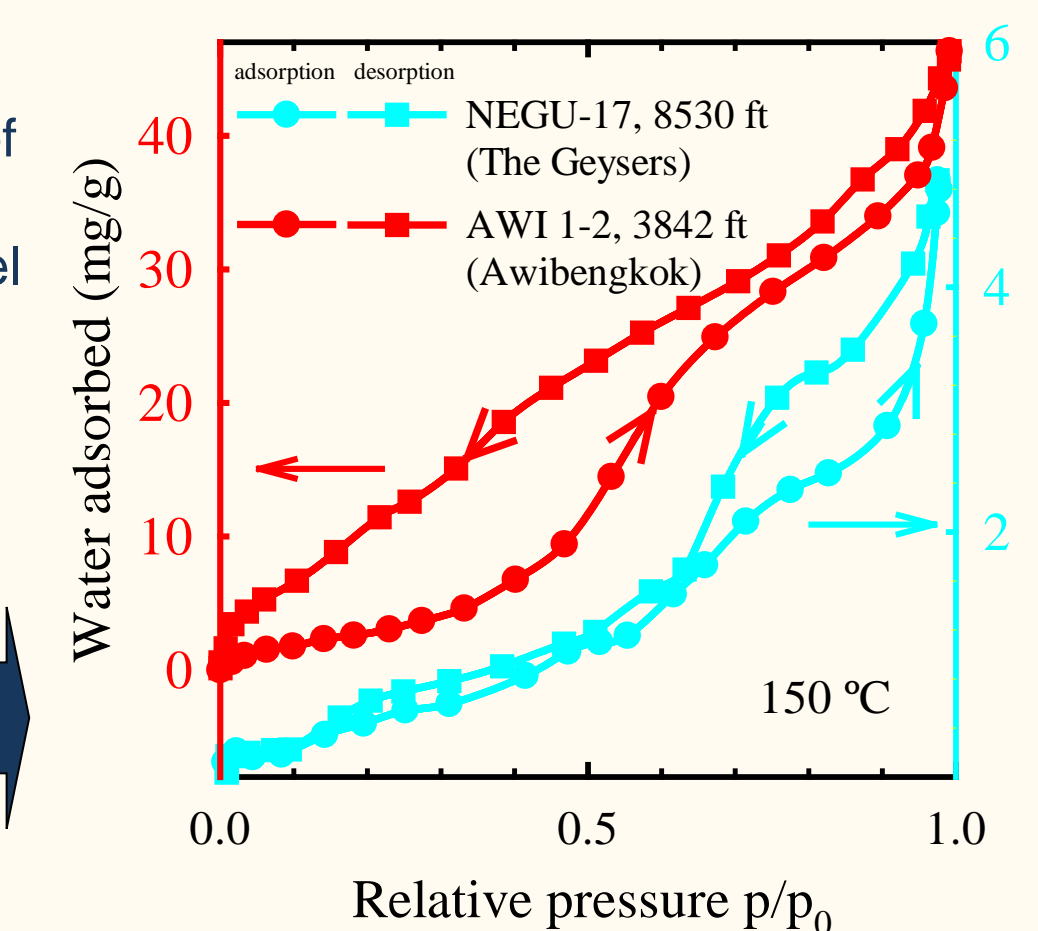
**Objective:** Determine the solute properties needed for accurate simulation of CO<sub>2</sub> behavior (solubility, reactivity, etc.) in concentrated brines

Activities and solubilities of aqueous solutes and isotherms of water adsorption in geothermal rocks, minerals, and engineered porous materials have been measured by the unique ORNL gravimetric method. The results over wide ranges of temperature and composition are used to characterize fluid-solid interactions and pore system geometries, develop universal property equations and validate molecular-level models.



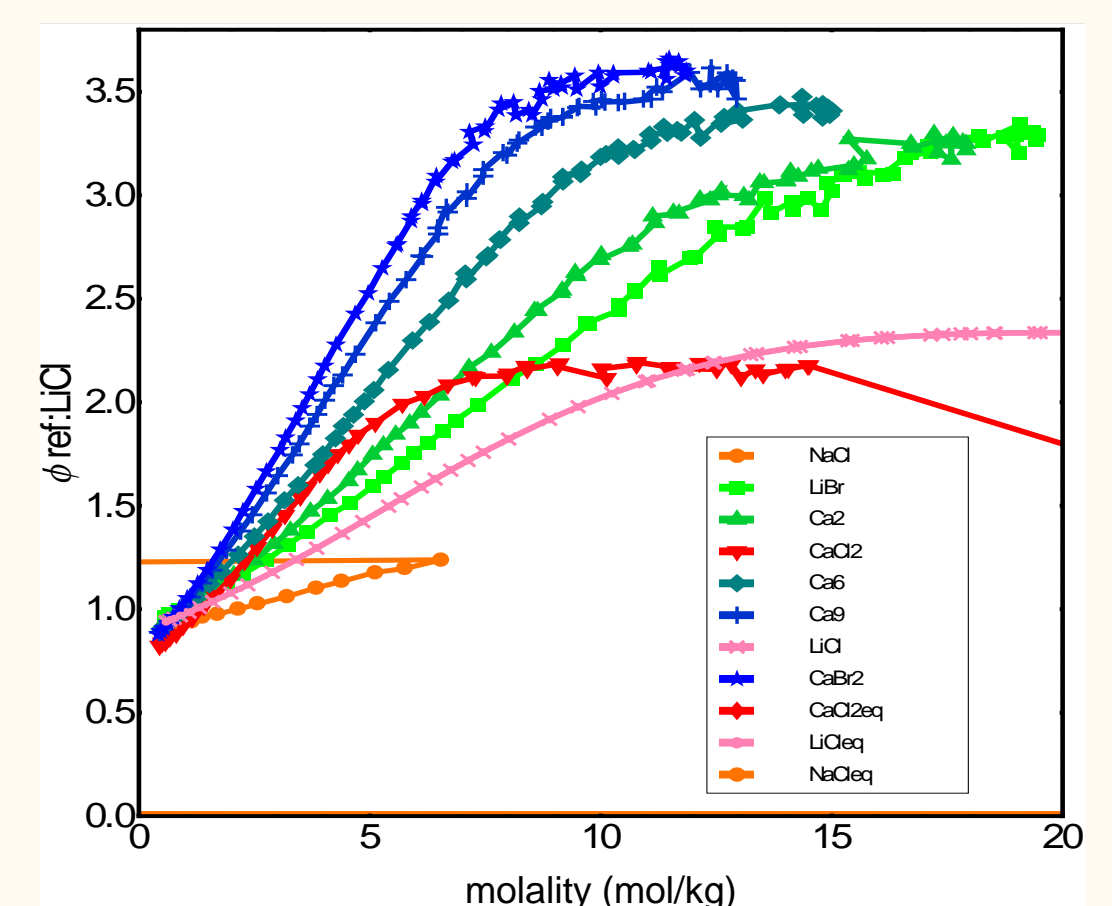
Osmotic coefficients of CaCl<sub>2</sub>(aq) calculated from a universal model (Gruskiewicz and Simonson, *J. Chem. Thermodyn.* 2005, 37,906-930).

Examples of isotherms of water adsorption/desorption in geothermal reservoir rocks.



Recent vapor pressure results: activities in concentrated LiBr + CaBr<sub>2</sub> + H<sub>2</sub>O:

Osmotic coefficients of LiBr, CaBr<sub>2</sub> and several LiBr + CaBr<sub>2</sub> mixtures (0.2, 0.5, and 0.8 mole fraction CaBr<sub>2</sub> shown) at 100 °C were determined from isopiestic vapor pressure measurements, using LiCl as the reference solution. The method also gives accurate solubilities and deliquescence/efflorescence points in multicomponent brines. The results enable development of semi-empirical temperature-dependent speciated thermodynamic models of multicomponent brines for accurate simulation of carbon capture and storage environments.



REFERENCES

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- Capobianco, R. M.; Gruskiewicz, M. S.; Bodnar, R. J.; Rimstidt, J. D. Conductivity Measurements on H<sub>2</sub>O-Bearing CO<sub>2</sub>-Rich Fluids. *J. Solution Chem.* 2015, 44(5), 934-962.

ACKNOWLEDGMENTS

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